

SYNTHESIS AND CHARACTERIZATION OF NATURAL RUBBER-SILICA COMPOSITE

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF NATURAL RUBBER-SILICA COMPOSITE. The composite of natural rubber-silica have been developed with a combination of silica (SiO_2) particles in irradiated natural rubber. This research was conducted with the aim to composite material with irradiated natural rubber as the matrix and silica particles as filler and to study the distribution of silica in the matrix as well as mechanical and physical properties. The results showed that the SiO_2 particles homogenously distributed across the surface of natural rubber matrix as the cluster. The particles are arranged as a cluster by using 3-aminopropyltriethoxysilane (APTES) as a coupling agent. Tensile strength, tensile modulus and elongation at break of composite materials have increased as the addition of SiO_2 on the composition of 9 to 12 percent weight in natural rubber. Additions of SiO_2 composition in the matrix will also increase the hardness of the composite. Structural analysis were performed using FT-IR and SEM. Composite of natural rubber- SiO_2 have a great potential to be applied as a natural rubber base materials mainly as protective products with higher performance.

Key words : Natural rubber, Silica, Composite, Coupling agent

ABSTRAK

SINTESIS DAN KARAKTERISASI KOMPOSIT DARI KARET ALAM-SILIKA. Komposit dari karet alam dan silika telah dikembangkan dalam penelitian ini. Tujuan dari penelitian ini adalah untuk membuat komposit berbasis karet alam teriradiasi sebagai matriks dan partikel silika sebagai pengisi (*filler*) dan untuk mempelajari distribusi dari partikel silika dalam matriks, sifat-sifat fisik dan mekanik dari komposit yang dihasilkan. Hasil penelitian menunjukkan bahwa partikel SiO_2 terdistribusi secara homogen pada permukaan dari matriks karet alam sebagai *cluster*. Partikel dari SiO_2 tertata sebagai *cluster* dengan menggunakan 3-aminopropyltriethoxysilane (APTES) sebagai *coupling agent*. Kekuatan tarik, modulus tarik, serta perpanjangan putus dari komposit mengalami kenaikan dengan bertambahnya komposisi SiO_2 (9 % w/w hingga 12 % w/w). Penambahan SiO_2 juga akan menaikkan tingkat kekerasan komposit. Analisis komposit dilakukan menggunakan FT-IR dan SEM. Hasil penelitian menunjukkan bahwa komposit karet alam-silika memiliki potensi yang baik untuk dipergunakan sebagai material berbasis karet alam terutama sebagai produk protektif dengan performa tinggi.

Kata kunci : Karet alam, Silika, Komposit, Coupling agent

INTRODUCTION

Advanced in producing high performance polymer based compositions will in future more likely result from the utilization of new mixtures of polymers and mixtures of polymers with reinforcing components, rather than from new polymer compositions. The term composites is generally applied to fiber reinforced engineering structural

materials, in which the fibers are continuous or long enough that they can be oriented to produce enhanced strength properties in one direction [1]. A composite structure is a combination of two or more different component resulting in material having better performance than each individual constituent [2]. Thus the material properties are a function of filler composition

which includes concentration, size, shape and distribution.

As new technologies continue to place increasingly stringent demands on the performance of polymeric materials, it is becoming clear that traditional polymer composites can not meet these requirements. As a result, new material composites are being developed, utilizing multifunctional nature of nano scale materials [3]. The interface between the composite components plays a defining role in the overall composite properties. The available interfacial area is increased by the dispersion of nano sized particles throughout the polymer matrix. So that the material is expected to have an improved properties such as its electrical properties, mechanical and other properties. The main characteristic of the beneficial use of filler particles is to use fewer products to reduce cost.

The wide spectrum of properties available to polymeric materials has afforded numerous practical applications ranging from common household goods to biomedical materials and aerospace components. This is because polymers generally have a distinctive behavior that is printable, lightweight, good insulators and cheap. Plastics, fibers, films, wires and rubber are some examples of polymers commonly used in industry.

In this study, the basic material used as the matrix is natural rubber or latex. Natural rubber is a natural polymer derived from isoprene monomer plant sap from *hevea brasiliensis* in family of *euphorbiaceae*. Natural rubber could be classified as an elastomer and it can be used as raw material for various types of finished goods such as rubber gloves. Natural rubber is a molecule with a backbone of *cis*-1,4-polyisoprene and color varies from yellow to dark brown, not resistant to hydrocarbon solvents and susceptible to oxidation and thermal degradation. Natural rubber is one of the most important elastomeric materials for diverse industrial applications. However, natural rubber by itself does not possess high enough modulus for most applications and needs to be reinforced with fillers and cross linked with curing agents.

Extensive studies have been carried out in the development of the performance of natural rubber products, such as using black carbon, calcium carbonate, the modified clay, and silica particles as filler materials in the natural rubber. Study of preparation and characterization of self assembled natural rubber/silica nanocomposites as well as effect of filler surface treatment properties of fly ash/natural rubber blend have been done [4,5]. Another research have been carried on covering properties of vulcanized rubber nanocomposites filled with nanokaolin and precipitated silica [6], the effect of filler on epoxidized natural rubber-alumina composite [7] and viscoelastic properties of natural rubber composites reinforced by defatted soy flour and carbon black co filler [8].

In this study, silica particles will be used as filler in natural rubber matrix. Silica is a compound of metal oxide which is widely available in nature, but its presence is bound with other compounds. The nature of the silica is hard, heat resistant and stable. Silica also has a wide surface area, large pore volume, and the ability to absorb another substance such as water, oil and radioactive materials. In general, silica is both hydrophilic and hydrophobic when bonded with other elements in accordance to the structure and morphology.

This research was conducted with the aim, to produce natural rubber based composite materials with silica particles as filler and to study the distribution of silica in the matrix as well as its mechanical and physical properties.

EXPERIMENTAL METHOD

The materials used are irradiated natural rubber with radiation dose of 15 kGy, silica type A275 obtained from UPN Surabaya, 3-aminopropyltriethoxysilane as a coupling agent, distilled water, 0.2 M NaOH and ethanol.

The equipments used in this study are: pipettes, measuring glass, spatula, mortar, sieve, High Energy Milling Machine (HEM) and mixer.

Natural rubber was irradiated priorly to obtain crosslinking to form three dimensional structure and physical properties changes. Silica as a filler first crushed using mortar and sieved using 400 mesh sieves. Silica powder pulverized again by using HEM for 8 hours. 3-aminopropyltriethoxysilane as a coupling agent as much as 10 percent weight mixed with the powder first silana with ethanol. Mixture should be stirred evenly then oven dried at 40 °C for 1 hour. After drying the mixture at silica and 3-APE dispersed into the water. Already dispersed silica with a pH of latex pH adjusted using NaOH. Furthermore, the dispersed silica was added to natural rubber with varied amounts of 3, 6, 9, 12 and 24 %w/w. The mixture was stirred by using a mixer for 30 minutes and then printed. Sample is left to dry at room temperature for several days, then washed and dried in an oven at a temperature of 70 °C for 1 hour. After drying the sample was ready for characterizations.

Characterization equipments used were X-Ray Diffractometer (XRD) Phillips PW 1710, PSA Delsa Nano C, Universal Testing Machine, and Fourier Transform Infra Red (FT-IR) Spectrometer.

Measurement of tensile strength, tensile modulus and elongation at break was done by using a Universal Testing Machine (UTM) following ASTM method D4102-9.

RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns for SiO₂ powders prior to milling process (0 hours) and after

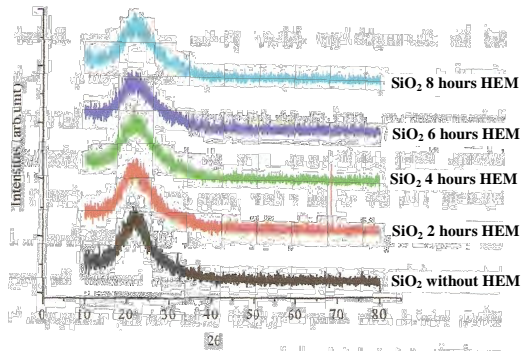


Figure 1. The XRD patterns of SiO_2 powders prior to milling process (0 hours) and after milling of 2, 4, 6 and 8 hours, respectively

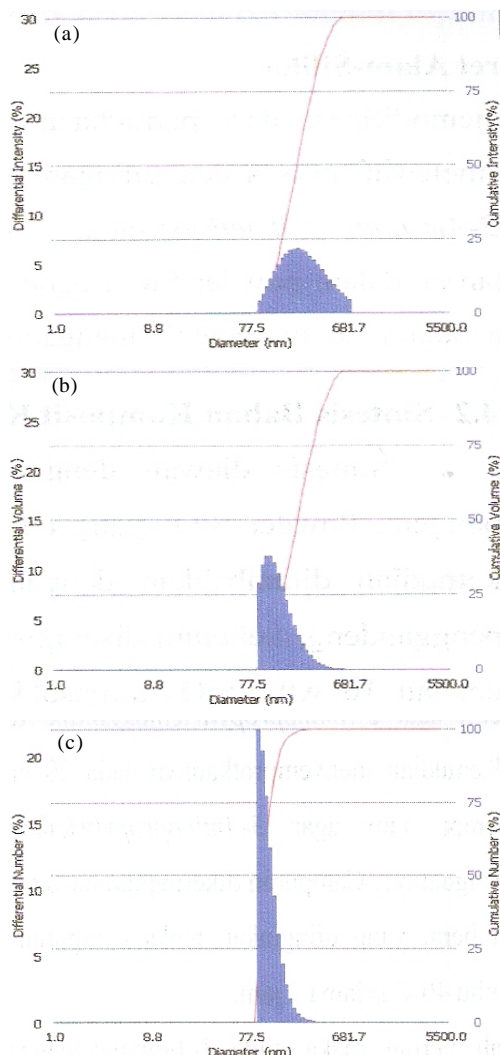


Figure 2. SiO_2 particle size distribution measured by using particle size analyzer (PSA).

consecutive milling time for 2, 4, 6 and 8 hours. From the diffraction pattern shown in Figure 1, it can be concluded that there is SiO_2 phase characterized by diffraction peaks at $2\theta = 10.76^\circ$ and 21.57° . Amorphous SiO_2 phase is dominating the diffraction pattern characterized by the absence of sharp peaks and the presence of broad diffraction peaks at angles $2\theta = 21.57^\circ$.

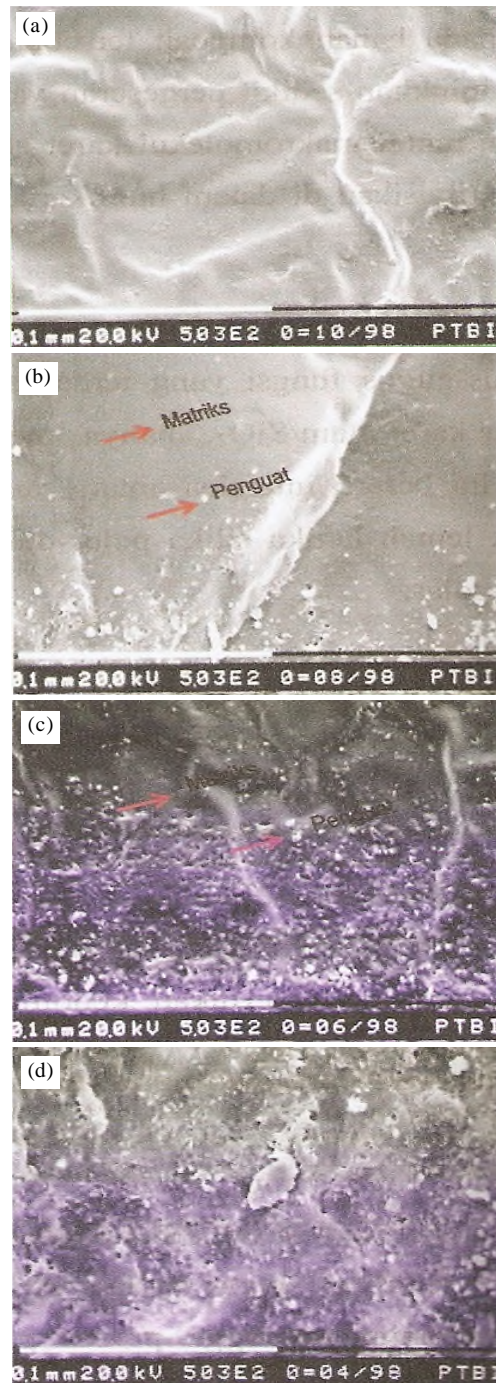


Figure 3. SEM images of natural rubber (a), natural rubber- SiO_2 composite with 9 % wt SiO_2 (b), natural rubber- SiO_2 composite with 12 % wt SiO_2 (c) and natural rubber- SiO_2 composite with 24 % wt SiO_2

SiO_2 particle size distribution measured by using particle size analyzer (PSA), are noted in Figure 2. The Figure 2 shows that the use of HEM can reduce the size of SiO_2 powder, which is 266 nm by using the intensity distribution analysis, using volume of distribution is 150 nm and using the sum distribution analysis is 117 nm.

A SEM image of natural rubber is shown in Figure 3. It displays the simple polymer network and there are no voids. The SEM image of natural

rubber-SiO₂ composites reveal homogenously distribution of SiO₂ particles as cluster. The dark image represents the natural rubber and the bright image corresponds to silica particles. From the SEM images the surface roughness increased with increasing filler up to 24 %. It can be observed that the agglomerates increase as the silica content was further added. This may due to the worsening wettability of matrix onto filler surface when ratio of fillers to natural rubber is too high.

Tensile Strength measurement as a function of the addition of SiO₂ in natural rubber shown in Figure 4. Based on these data we can conclude that the tensile strength tends to increase with increasing SiO₂ content until 12 % in natural rubber. By increasing the filler, the chemical bonding between polymer and filler increased, so the force applied can be distributed homogenously by the filler.

The maximum tensile strength was obtained with the SiO₂ composition in natural rubber as much as 12 % with a tensile strength of 19.91 MPa. In SiO₂ addition as many as 24 % tensile strength decreasing compared to tensile strength at 12 % filler addition, because the filler particles are no longer adequately separated or wetted by rubber phase. This result is in agreement with the SEM image obtained.

Tensile modulus measurement at 600 % elongation as effect of SiO₂ addition in natural rubber shown in Figure 5. Mechanical properties of a material can be seen from the modulus of elasticity. The greater the modulus of elasticity, the better mechanical properties

of the materials because the material is not easily deformed. Tensile modulus is increasing by the addition of SiO₂ for 12 to 24 %. This strengthening anticipated for dispersing the filler has done well so homogenously distributed in the matrix.

Elongation at break of natural rubber-SiO₂ composite increases with increasing composition of SiO₂ until 12 % and then decreases at 24 %, as shown in Figure 6. At composition of 12 % SiO₂, interaction between filler surface with natural rubber as matrix is strong. This is due to cross-linking between natural rubber. But at the addition of 24 % SiO₂ elongation at break of the composites decrease, caused by slip between SiO₂ particles in natural rubber matrix which weakens the bond and easily broken.

As usually conceived, hardness is a composite property combining concept of resistance to penetration, scratching, marring and so on. Most hardness tests for plastics are based on resistance to penetration by an indenter pressed into the plastic under constant load. Effect of SiO₂ content as filler to composite hardness is shown in Figure 7.

Based on Figure 7 in above, it is concluded that increasing the SiO₂ content in the matrix, will increase the composite hardness. This increasing may be attributed to higher crosslink and good distribution of fillers in the natural rubber matrix.

The FT-IR spectra of SiO₂, natural rubber and natural rubber-SiO₂ composite with addition of 9 wt% SiO₂ could be seen in Figure 8, Figure 9 and Figure 10 respectively. The peak at 1105 cm⁻¹ could be ascribed to

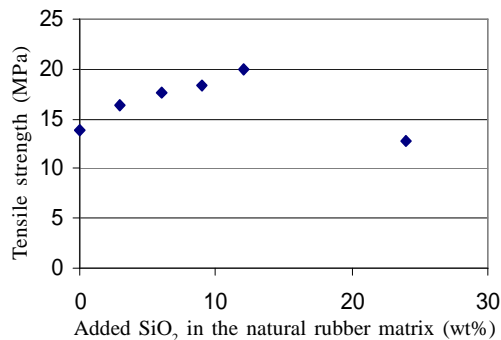


Figure 4. Graph of tensile strength as addition of SiO₂ in the natural rubber matrix

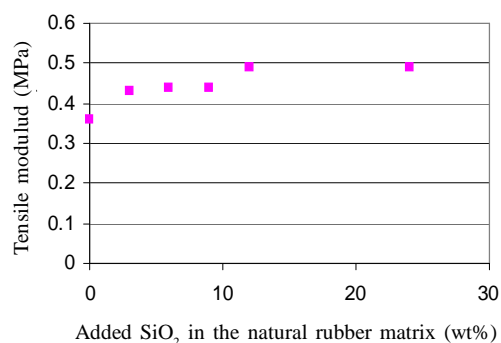


Figure 5. Graph of tensile modulus as addition of SiO₂ in the natural rubber matrix

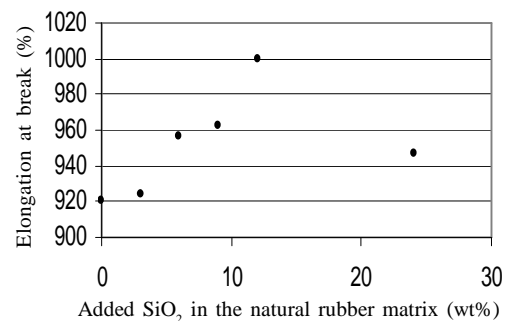


Figure 6. Graph of elongation at break of natural rubber-SiO₂ composites as addition of SiO₂ in the matrix

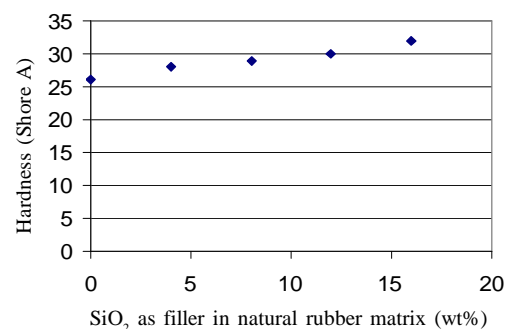


Figure 7. Effect of SiO₂ as filler to composite hardness

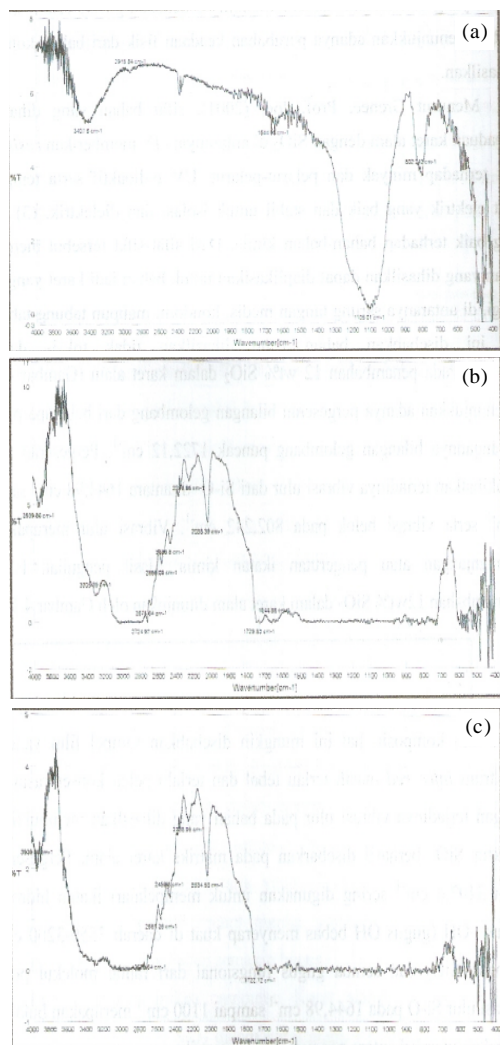


Figure 8. (a) The FT-IR spectra of SiO₂, (b) The FT-IR spectra of natural rubber and (c) The FT-IR spectra of natural rubber-SiO₂ composite

the stretching vibration of Si-O band. While the 3940 cm⁻¹, 3306 cm⁻¹, 2038 cm⁻¹ peak were the relative to C-H, O-H and C = C groups, respectively. The FT-IR

spectra of natural rubber-SiO₂ composite in Figure 8(c) are different to the Figure 8(a) and Figure 8(b). The difference of FT-IR spectra is loss peak at 1645 cm⁻¹ and wave numbers shift occurred from 1730 cm⁻¹ to 1722 cm⁻¹. Wave number shift is caused by the interaction of SiO₂ with natural rubber that involving chemical bonding between polymer and filler.

CONCLUSIONS

Natural rubber as the matrix has good elasticity, have been dispersed silica into it to form a composite with the addition of 3-aminopropyltriethoxysilane as coupling agent has good mechanical properties.

Additions of SiO₂ into the natural rubber as much as 12 wt% produce optimum mechanical properties namely tensile strength of 19.91 MPa, tensile modulus at 600% elongation of 3.48 MPa and elongation at break of 1000 %.

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